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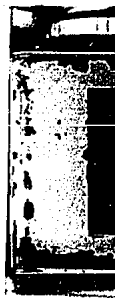

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PHOSPHONOETHYLATION

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Submitted by Academician A. Ye. Arbuzov, 27 Jun 1951

In previously published reports (1) we described a new method of synthesizing derivatives of phosphonic esters. This method consists of the addition of dialkyl phosphorous acids to unsaturated electrophilic reagents such as unsaturated ketones, aldehydes, acids and their esters, and esters of vinyl alcohols. The method we described is extremely simple to carry out, is practicable in regard to the starting materials used, and, in most cases, supplies a high yield of addition products. During the past few years, we have synthesized with the aid of this method a large number of heretofore unknown esters of ketophosphonic, unsaturated hydroxyphosphonic, cyanophosphonic, phosphonocarboxylic acids, and some others. In the expansion and development of these investigations in this report, it is shown that the simplest of the few previously known α,β-unsaturated phosphonic esters -- the ethyl ester of vinylphosphonic acid -- can be used successfully as the electrophilic unsaturated reagent. It must be pointed out that vinylphosphonic esters and their derivatives have been studied only very little up to now, and that, in particular, the addition reactions with them have not been investigated at all.

In the course of the work, it was established that vinylphosphonic ester is sufficiently available and -- another important feature -- is a sufficiently stable compound which will not polymerize if left standing for several days at room temperature, or during vacuum distillation, or during heating over a water bath for several hours. Even the first experiments conducted with vinylphosphonic ester showed that it is an extremely active compound which will easily combine not only with dialkylphosphorous acids, but also with a number of other nucleophilic reagents such as ammonia, amines, the esters of malonic, cyanoacetic, and acetoacetic acid, their homologs, benzyl cyanide, and others. We have discovered a new addition reaction between nucleophilic reagents and vinylphosphonic acid, which, in addition to being of theoretical interest, has definite significance in the synthesis of various phosphonic ester derivatives.

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To clarify the nature of the process, we found it expedient to call the reaction we discovered phosphonoethylation, in analogy to the well-known and widely used cyanoethylation, since a phosphonoethyl group is introduced into various organic compounds.

The addition of dialkylphosphorous acid to vinylphosphonic ester was carried out in the presence of alcoholates of alkali metals. To prevent an exchange of radicals between alcoholate and dialkylphosphorous acid, both these reagents were taken with the same radical, as in previous work. The reaction proceeded very easily. The following addition products of dimethylphosphorous, diethylphosphorous, di-isobutylphosphorous, and dibutylphosphorous acid with vinylphosphonic ester were obtained in yields of approximately 60% of the theoretical:

1-dimethylphosphono-2-diethylphosphonoethane (bp 158-160°C/2mm, n_D^{20} =1.4430, d_4^{20} = 1.2075)

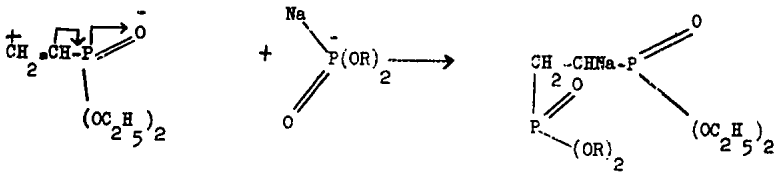
1,2-di(diethylphosphono)ethane (bp 164-165°C/2 mm, n_D^{20}= 1.4410, d_4^{20}=1.1376)

1-di-isobutylphosphono-2-diethylphosphonoethane (bp 183-184°C/2 mm, n_D^{20}=1.4391, d_4^{20} = 1.0471)

1-dibutylphosphono-2-diethylphosphonoethane (bp 197-199°C/2 mm, n_D^{20} = 1.4430, d_4^{20} = 1.0681

1,2-di(diethylphosphono) ethane which we obtained is completely identical, according to its constants, with the product obtained by Ford-Moore (2) in the action of triethyl phosphite on dibromoethane. The mechanism of the addition reaction can be represented by the following general scheme:

$$(RO_2)POH + RONa \rightleftharpoons (RO)_2PONa + ROH$$



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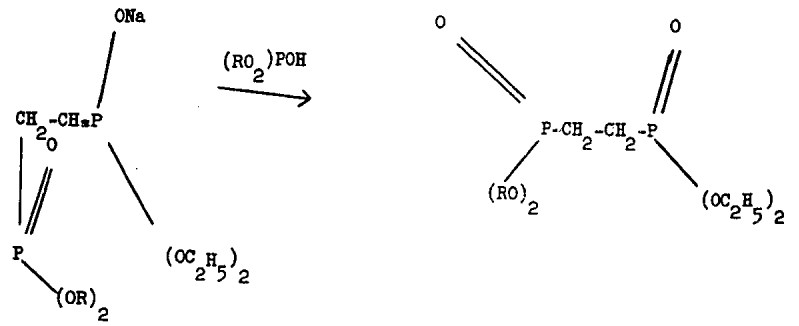
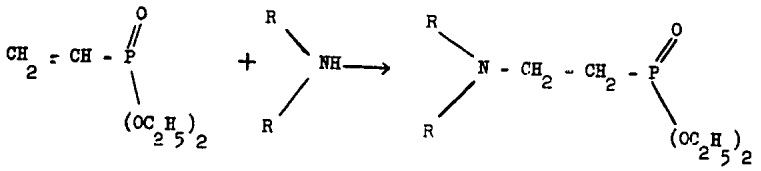


where R = CH_3, C_2H_5, i-C_4H_9, or n-C_4H_9.

Ammonia and amines usually add to vinylphosphonic ester in the presence of sodium ethylate; in some cases, the reaction also proceeds very successfully in the absence of catalysts. The addition of ammonia in an alcohol solution and in the presence of sodium ethylate furnished a 67% yield of β- diethylphosphonoethylamine, bp 93-95°C/4 mm, n_D^{20} = 1.4270, d_4^{20} = 1.0515.

Dimethylamine is added to vinylphosphonic ester in the absence of a catalyst. Already during the mixing of the reagents a fairly considerable warming up of the reaction mixture can be observed. The yield of the addition product, the ethyl ester of β- dimethylphosphono ethyldimethylamine, after letting the mixture stand at room temperature for 24 hr, was 83%. The product has a bp of 103-104°C/4 mm, n_D^{20} = 1.4345, d_4^{20} = 1.0157. Analogously, upon the addition of piperidine to vinylphosphonic ester, β- diethylphosphonoethylpiperidine with a bp of 135-137°C/3 mm, n_D^{20} = 1.0514, d_4^{20} = 1.0154 was obtained in a yield of 52.6%. Upon the addition of aniline, β- diethylphosphonoethylaniline, bp = 145-150°C/6 mm, n_D^{20} = 1.4910, d_4^{20} = 1.0947 was obtained. However, the yield of the latter was insignificant. The formation of a large quantity of low-boiling fractions was observed. The reaction can be expressed by the following general scheme:



where R = H, CH_3, C_6H_5, or others.

We further showed that malonic, cyanoacetic, and acetoacetic esters, their homologs, and also benzyl cyanide, in most cases very easily add to vinylphosphonic ester in the presence of alcoholates of basic metals. The esters of the following compounds were obtained, with yields of 78-86%, as a result of the addition of malonic ester, methyl-, ethyl-, propyl-, and n-butylmalonic esters, respectively:

β -diethylphosphonoethylmalonic acid (bp 158-159°C/1 mm, n_D^{20} = 1.4420, d_4^{20} = 1.1316)

β -diethylphosphonoethylmethylmalonic acid (bp 175-177°C/4 mm, n_D^{20} = 1.4400, d_4^{20} = 1.1021)

β -diethylphosphonoethylethylmalonic acid (bp 162°C/2.5 mm, n_D^{20} = 1.4423, d_4^{20} = 1.0925)

β -diethylphosphonoethylpropylmalonic acid (bp 175-176°C/2 mm, n_D^{20} = 1.4425, d_4^{20} = 1.0782)

β -diethylphosphonoethyl-n-butylmalonic acid (bp 185-186°C/2.5 mm, n_D^{20} = 1.4432, d_4^{20} = 1.0640)

Addition to vinylphosphonic ester of cyanoacetic acid in equimolecular quantity yielded two products:

β-diethylphosphonoethylcyanoacetic ester (bp 166-167°C/2 mm, n_D^{20} = 1.4430, d_4^{20} = 1.0740)

di(β-diethylphosphono ethyl) cyanoacetic ester (bp 227°C/2 mm, n_D^{20} = 1.4540, d_4^{20} = 1.3830)

The total yield of these two products was 63%.

The addition of cyanoacetic ester homologs to vinylphosphonic ester proceeded more smoothly. The ethyl esters of the following compounds were obtained in yields between 75 and 90%:

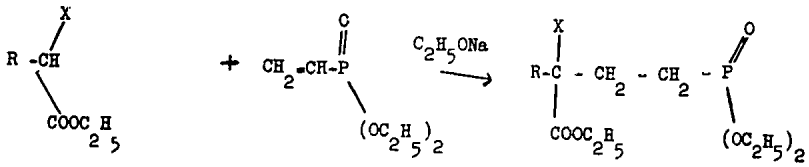
β-diethylphosphonoethylmethylcyanoacetic acid (bp 165-166°C/3.5 mm, n_D^{20} = 1.4430, d_4^{20} = 1.0989)

β-diethylphosphonoethylethylcyanoacetic acid (bp 173-174°C/2 mm, n_D^{20} = 1.443, d_4^{20} = 1.0702)

β-diethylphosphonoethyl n-butylcyanoacetic acid (bp 177-178°C/3 mm, n_D^{20} = 1.4460, d_4^{20} = 1.0564)

Addition of acetoacetic ester and its homologs to vinylphosphonic ester proceeds considerably less smoothly than the addition of malonic and cyanoacetic esters and their homologs. Besides the addition products, a large quantity of low-boiling fractions, with yields of 20-25%, was obtained. β-diethylphosphonoethylcyanoacetic and β-diethylphosphonoethylpropylacetoacetic ester were isolated. Upon addition of benzyl cyanide to vinylphosphonic ester, the basic reaction product was di(β-diethylphosphonoethyl)benzyl cyanide (bp 247-248°C/2 mm, n_D^{20} = 1.4940). β-diethylphosphonoethylbenzylcyanide was formed only in very small quantities.

All reactions discussed above can be described by the following general scheme:



where X = $COOC_2H_5$, CH_3CO, CN, or C_6H_5, and R = H, CH_3, C_2H_5, n-C_3H_7, or n-C_4H_9.

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2. A. Ford-Moore and I. H. Williams, Journ. Chem. Soc., 1947, p 1465.

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